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(54) PRODUCTION OF COMPLEX SILICA FINE PARTICLE

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method for readily producing complex silica fine particles having excellent affinity for matrix resins and free from scattering of physical properties.
SOLUTION: This method for producing complex silica particles comprises obtaining the complex silica particles by combining spherical fine particles with an organic polymer in a complex process. In the complex process, spherical fine particles are combined with the organic polymer by hydrolyzing and condensing the organic polymer (P) having at least one polysiloxane group per molecule and containing at least one Si-OR1 group (R1 is at least one kind of group selected from hydrogen atom, an alkyl group and an acyl group and the alkyl group and the acyl group may be substituted; plural R1s may be mutually different when plural R1s exist in one molecule) in a polysiloxane group in a dispersion in which spherical silica fine particles are dispersed.

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* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] Are the method of compound-izing a spherical silica particle with organic polymer, and obtaining a compound silica particle, and this compound-ized process in dispersion liquid which distributed said spherical silica particle at least one polysiloxane radical per molecule -- having -- and the inside of said polysiloxane radical -- at least one Si-OR1 radical (R1 -- a hydrogen atom --) radical;R1 by which it is at least one sort of radicals chosen from an alkyl group and an acyl group, and said alkyl group and acyl group may be replaced a case where more than one are in 1 molecule -- two or more R1 You may differ mutually. A manufacture method of a compound silica particle characterized by what is been the process which compound-izes said spherical silica particle by hydrolyzed and condensing organic polymer (P) to contain.
[Claim 2] A compound silica particle obtained by manufacture method according to claim 1.
[Claim 3] A compound silica particle dispersing element which a compound silica particle according to claim 2 comes to distribute in dispersion liquid.
[Claim 4] A plastic film which a compound silica particle according to claim 2 comes to distribute in matrix resin.
[Claim 5] A mat agent which comes to contain a compound silica particle according to claim 2.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] This invention relates to a compound silica particle useful as the filler used for a film, a molding material, a coating, fiber, sensitive material, etc., a mat agent, a surface treatment agent, a solid lubricant, etc., its manufacture method and a dispersing element, and amelioration of the use of a plastic film etc.
[0002]
[Description of the Prior Art] Before, various non-subtlety particles are used as a mat agent aiming at the anti blocking nature grant to the slipping agent of various plastic films, sensitive material, various plastic films, etc. In these uses, since it is so effective that the touch area of a non-subtlety particle and the contact surface where a non-subtlety particle contacts is small, as for the configuration of a non-subtlety particle, it is desirable that it is spherical. However, the non-subtlety particle was difficult for generally compatibility with the matrix resin which constitutes a plastic film, and the binder resin used for making a mat agent fix fixing a non-subtlety particle low by **, matrix resin, and binder resin ("matrix resin and binder resin" "being called matrix resin etc." hereafter). Furthermore, the touch area with matrix resin etc. became it small that the configuration was spherical, and there was a problem of dropping out of these easily.
[0003] In order to solve the problem of the compatibility of a non-subtlety particle, matrix resin, etc., the compound-ized method shown below is proposed. For example, compound-izing the silica particle whose particle diameter is 5-300nm by silyl etherification polymer is indicated by JP,3-271114,A. Tsubokawa and others did the radical polymerization of these radicals, or made the silyl radical content polymer coupling agent react to said silica particle after introducing a polymerization nature functional group and a polymerization initiation radical into the silica particle front face whose particle diameter obtained by the gaseous-phase method is dozens of nm, and it has reported carrying out the graft of the organic polymer to the front face of a silica particle ("front face" the 28th volume, No. 4, the 286-298th page, 1990). It is indicated by JP,5-115772,A that particle diameter performs an emulsion polymerization after introducing a polymerization nature functional group into the front face of the silica particle obtained by the gaseous-phase method which is dozens of nm, and graft-izes the front face of a silica particle by polymer. After processing beforehand the colloidal silica front face whose particle diameter is 10-5000nm by the coupling agent, the method of compound-izing by acid radical content polymer is indicated by JP,4-180921,A. Moreover, Yoshinaga and others has reported the example which compound-izes a mono dispersion

silica particle by alkoxy silyl radical content polymer (the "Society of Fiber Science and Technology, Japan" the 49th volume, No. 3, the 130-136th page, 1993).
[0004]
[Problem(s) to be Solved by the Invention] When this invention persons retest the above-mentioned official report or the compound-ized method given in reference, by these compound-ized methods Since it is indispensable to perform desiccation processing after compound-izing as for all, and it is difficult to control desiccation processing conditions to accuracy when performing desiccation processing, The condensation of a compound particle and the bridge formation between the compound particles by organic polymer arose, variation was seen by the particle diameter of a compound particle etc., and it turned out that repeatability is low.
[0005] Then, the technical problem of this invention is offering the compound silica particle which has the compatibility which was excellent to matrix resin etc., and does not have variation in physical properties, and the method of manufacturing this compound silica particle easily. Another technical problem of this invention is offering the compound silica particle dispersing element which is excellent in handling nature.
[0006] Still more nearly another technical problem of this invention is offering the plastic film which there are no omission of a compound silica particle, has sufficient slipping nature, and was excellent in abrasion resistance. Still more nearly another technical problem of this invention is offering the mat agent which gives the outstanding anti blocking nature and does not drop out easily.
[0007]
[Means for Solving the Problem] Since this invention persons did not need to perform a desiccation process when a silica particle was compound-ized by specific organic polymer, as a result of inquiring wholeheartedly, in order to solve the above-mentioned technical problem, they acquired knowledge that a compound silica particle could be manufactured without producing condensation and bridge formation, and reached this invention.
[0008] Namely, a manufacture method of a compound silica particle of this invention Are the method of compound-izing a spherical silica particle with organic polymer, and obtaining a compound silica particle, and this compound-ized process in dispersion liquid which distributed said spherical silica particle at least one polysiloxane radical per molecule -- having -- and the inside of said polysiloxane radical -- at least one Si-OR1 radical (R1 -- a hydrogen atom --) radical;R1 by which it is at least one sort of radicals chosen from an alkyl group and an acyl group, and said alkyl group and acyl group may be replaced a case where more than one are in 1 molecule -- two or more R1 You may differ mutually. By hydrolyzing and condensing organic polymer (P) to contain, it is characterized by what is been the process which compound-izes said spherical silica particle.
[0009] A compound silica particle of this invention is a compound silica particle obtained by above-mentioned manufacture method. A compound silica particle dispersing element of this invention is a dispersing element which the above-mentioned compound silica particle comes to distribute in dispersion liquid. A plastic film of this invention is a film which the above-mentioned compound silica particle comes to distribute in matrix resin.
[0010] A mat agent of this invention comes to contain the above-mentioned compound silica particle.
[0011]
[Embodiment of the Invention]
[A compound silica particle and its manufacture method] It is characterized by for the manufacture method of the compound silica particle of this invention being a method of compound-izing a spherical silica particle with organic polymer, and obtaining a compound silica particle, and this compound-ized process being a process which compound-izes said spherical silica particle by hydrolyzing and condensing organic polymer (P) in the dispersion liquid which distributed said spherical silica particle.
[0012] About the spherical silica particle used by this invention, if the configuration is spherical, it will not be limited especially. The thing as used in the field of this invention which means a near configuration as spherical spherically [the shape of a true ball, an egg, etc.], for example, has the aspect ratio (ratio of the diameter of the shortest of a particle and the diameter of the longest) of a particle within the limits of 0.5-2 is said. Since the aspect ratio of a particle can give the anti blocking nature which was excellent when the slipping nature of the plastic film containing the compound silica particle obtained as it is 0.7-1.5 improved or the compound silica particle obtained was used as a mat agent, it is desirable.
[0013] Although there is especially no limit about the particle diameter of a spherical silica particle and the thing of all particle diameter can be used, in a compound-ized process, from the ease of carrying out of control of a reaction, a thing with a mean particle diameter of 5nm - 10 micrometers is 0.1-10 micrometers desirable still more preferably, and it is 0.3-5 micrometers most preferably. It is not limited especially about the process of a spherical silica particle, and may be obtained by which method of scorification, a melting atomizing process, the depositing method, the alkoxide method, a suspension method, interfacial polymerization, the neutralization processes, etc. It is desirable in order for many alkoxy groups to which the spherical silica particle obtained especially by the alkoxide

method which uses a tetramethoxy silane etc. as a raw material tends to react with the below-mentioned organic polymer (P) to exist in the front face of a spherical silica particle.

[0014] Although there is especially no limit about the particle size distribution of a spherical silica particle, it is 30% or less most preferably 40% or less desirable still as more preferably as the coefficient of variation of particle diameter being 50% or less. If the compound silica particle from which the particle size distribution to which the coefficient of variation of particle diameter exceeds 50% is acquired using a large spherical silica particle is included in the Plastic solid of a plastic film etc. as a filler, physical properties, such as the smooth nature of the front face of the Plastic solid and slipping nature, may fall. Moreover, even if it uses the compound silica particle obtained as a mat agent, sufficient anti blocking nature may be unable to be given.

[0015] Although the spherical silica particle may contain other inorganic oxides other than a silica, 20 or less % of the weight of the whole spherical silica particle of the content of the inorganic oxide of others [ease / of carrying out / of acquisition of a spherical silica particle] is desirable, its 10 or less % of the weight is more desirable, and its 5 or less % of the weight is the most desirable. The organic radical and the hydroxyl group may contain the spherical silica particle. An organic radical here is at least one sort chosen from the with a carbon number of 20 or less alkyl group which may be replaced, a cycloalkyl radical, and an aryl group **** aralkyl radical. Ten or less % of the weight of the whole spherical silica particle of the content of the organic radical contained in a spherical silica particle is desirable, its 5 or less % of the weight is more desirable, and its 2 or less % of the weight is the most desirable.

[0016] It consists of an organic chain and a polysiloxane radical, and has at least one polysiloxane radical per molecule, and the organic polymer (P) used for this invention is at least one Si-OR1 in said polysiloxane radical. It has the structure containing a radical. Especially the structure of an organic chain is not limited in organic polymer (P). Organic polymer (P) has the work which gives the outstanding compatibility over matrix resin etc. to a spherical silica particle. The joint gestalt of a polysiloxane radical and an organic chain is Si-C association. Here, there is a possibility that this joint gestalt may be easily cut by hydrolysis, exchange reaction, etc. as a joint gestalt is Si-O-C association etc.

[0017] It is not what will be restricted especially if it dissolves in the organic solvent and water which are mentioned later as structure of organic polymer (P). For example, polymer in which the polysiloxane radical carried out the graft to the organic chain, polymer which the polysiloxane radical combined with both organic chain both [one of the two or], Or the polymer which the organic chain (two or more organic chains may be the same, or may differ) of the shape of two or more shape of a straight chain and branching combined by using a polysiloxane radical as a core is mentioned.

[0018] Organic chains are portions other than a polysiloxane radical in organic polymer (P) here. Since that to which a carbon atom is made into a subject, the content occupies 50-100-mol% of the organic whole chain, and elements, such as N, O, S, Si, and P, occupy the remainder is obtained easily, the element which constitutes the principal chain in an organic chain is desirable. As an example of the resin which constitutes an organic chain, polyester [, such as polyolefine; polyvinyl chloride; polyvinylidene chloride; polyethylene terephthalate,], such as acrylic resin (meta); polystyrene; polyvinyl acetate; polyethylene and polypropylene, these copolymers, resin which denaturalized in part, etc. are mentioned, for example. The resin which constitutes an organic chain especially is desirable in order to tend to manufacture organic polymer (P) as it is at least one sort chosen from acrylic resin (meta) and polyester.

[0019] Said Si-OR1 Few R1 O sets of a radical are a functional group in which hydrolysis and/or condensation are possible, and even if there are per organic (polymer P) 1 molecule, they are one piece. As for R1 O set, it is desirable that they are an average of five or more pieces, and it is more desirable that they are 20 or more pieces. The reacting point when hydrolyzing and condensing organic polymer (P) increases, and it becomes possible to strengthen association with a spherical silica particle more, so that there are many R1 O sets. It is R1 here. It is at least one sort of radicals chosen from a hydrogen atom, an alkyl group, and an acyl group, and said alkyl group and acyl group are a radical which may be replaced. Although especially the carbon number is not limited about an alkyl group and an acyl group, R1 O set hydrolysis speed is quick, and in order to be able to manufacture a compound silica particle efficiently easily, the alkyl group and acyl group of carbon numbers 1-5 are desirable. As an alkyl group of carbon numbers 1-5, alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, the 2nd class butyl, the 3rd class butyl, and a pentyl radical, are mentioned, for example. As an acyl group of carbon numbers 1-5, acyl groups, such as an acetyl group and a propionyl radical, are mentioned, for example. The radical by which it comes to replace 1 of the hydrogen atom which the above-mentioned alkyl group and an acyl group have, or two pieces or more with halogens, such as acyl group; chlorine, such as alkoxy group; acetyl groups, such as a methoxy group and an ethoxy radical, and a propionyl radical, and a bromine, etc. as the alkyl group replaced and an acyl group replaced, for example is mentioned. R1 When more than one are in 1 molecule, it is two or more R1. It may be mutually the same or you may differ. Especially, it is R1. At least one sort chosen from a hydrogen

atom, a methyl group, and an ethyl group is desirable, and a methyl group is the most desirable. This is because the reaction rate of R1 O set hydrolysis and condensation becomes still quicker and a compound silica particle can be manufactured efficiently easily.

[0020] A polysiloxane radical is Si-OR1 which the R1 O set combined with Si atom. It has one or more radicals and two or more Si atoms are the radicals which it comes to connect by polysiloxane association (Si-O-Si association) the shape of a straight chain, and in the shape of branching. Although especially the number of Si atom which this polysiloxane radical has is not necessarily limited, it is the average per polysiloxane radical, it is the point which can contain many R1 O radicals mentioned above, and 11 or more pieces are [its three or more pieces are desirable, its seven or more pieces are still more desirable, and] the most desirable [the number]. As such a polysiloxane radical, the poly methyl methoxy siloxane radical, a poly ethyl methoxy siloxane radical, a poly methylethoxy siloxane radical, a poly ethyl ethoxy siloxane radical, a polyphenyl methoxy siloxane radical, a polyphenyl ethoxy siloxane radical, etc. are mentioned, for example.

[0021] Furthermore, as for Si atom in a polysiloxane radical, having combined only with the R1 O set is [everything but association with an organic chain, and polysiloxane association (Si-O-Si association)] desirable. In such a case, it is because the ionicity of Si atom increases more, the reacting point in organic polymer (P) increases more while the speed of R1 O set hydrolysis and condensation becomes quicker and can manufacture a compound silica particle efficiently easily as a result, and the outstanding compatibility over matrix resin etc. can be given to a compound silica particle. As such a polysiloxane radical, a poly dimethoxy siloxane radical, a poly diethoxy siloxane radical, a PORIJI isopropoxy siloxane radical, a Pori n-butoxy siloxane radical, etc. are mentioned, for example.

[0022] Although especially the molecular weight of organic polymer (P) is not limited, the number average molecular weight is 200,000 or less preferably, and is 50,000 or less still more preferably. It may not dissolve in the dispersion liquid which will be later mentioned if molecular weight is too high. Although the method of (1) - (4) which can manufacture organic polymer (P) by the well-known method conventionally, for example, is shown below is mentioned, it is not limited to these.

[0023] (1) How to do the cohydrolysis and condensation of the obtained polymer (**), the silane compound (H) mentioned later, and/or its derivative, after carrying out the radical (**) polymerization of the radical polymerization nature monomer under existence of a silane coupling agent which has a double bond radical and a sulfhydryl group.

(2) How to carry out the radical (**) polymerization of the bottom radical polymerization nature monomer of existence of the cohydrolysate which was able to obtain a silane coupling agent which has a double bond radical and a sulfhydryl group, the silane compound (H) mentioned later, and/or its derivative after condensing, a cohydrolysis and, and a condensate (for it to abbreviate to a polymerization nature polysiloxane hereafter).

[0024] (3) How to do the cohydrolysis and condensation of the obtained polymer, the silane compound (H) mentioned later, and/or its derivative, after making the polymer which has a silane coupling agent which has reactant radicals, such as a double bond radical, an amino group, an epoxy group, and a sulfhydryl group, said reactant radical, and a radical which reacts react.

(4) The method to which the polymer which has cohydrolysate and a condensate which have said reactant radical which was able to obtain a silane coupling agent which has reactant radicals, such as a double bond radical, an amino group, an epoxy group, and a sulfhydryl group, the silane compound (H) mentioned later, and/or its derivative after condensing, a cohydrolysis and, said reactant radical, and a radical which reacts is made to react.

[0025] (2) is desirable at the point that organic polymer (P) can be more easily obtained also in the above. As a silane coupling agent which has reactant radicals, such as a double bond radical mentioned above, an amino group, an epoxy group, and a sulfhydryl group, vinyltrimetoxysilane, methacryloxy propyl trimethoxysilane, aminopropyl trimethoxysilane, 2-aminoethyl aminomethyl trimethoxysilane, glycidoxy propyltrimethoxysilane, mercaptomethyl trimethoxysilane, mercapto propyltrimethoxysilane, etc. are mentioned, for example.

[0026] As a silane compound (H), for example Methyltriacetoxysilane, Acyloxy silane compounds, such as a dimethyl diacetoxy silane, trimethyl acetoxysilane, and tetra-acetoxysilane; A tetramethoxy silane, A tetra-ethoxy silane, tetra-isopropoxysilane, tetra-butoxysilane, Methyl trimetoxysilane, phenyl trimethoxysilane, phenyl triethoxysilane, Alkoxysilane compounds, such as dimethoxy dimethylsilane, dimethoxymethyl phenylsilane, a trimethyl methoxy silane, a trimethyl ethoxy silane, dimethyl diethoxysilane, and dimethoxy diethoxysilane, etc. are mentioned. Moreover, as an example of the derivative of a silane compound (H), hydrolysis, the condensate, etc. of the above-mentioned silane compound (H) are mentioned.

[0027] An alkoxysilane compound is [that it is especially easy to receive as a raw material] desirable among silane compounds (H). moreover, hydrolysis / condensation speed is quick in a silane compound (H) and its derivative being a tetra-alkoxysilane compound and its derivative, the front face of a spherical silica particle is compound-ized efficiently easily, and a compound silica particle can be manufactured -- it is desirable.

[0028] By the manufacture method of the compound silica particle of this invention, in the dispersion liquid which

distributed the spherical silica particle, compound-ization of a spherical silica particle is performed and a compound silica particle is obtained. The dispersion liquid which distributed the spherical silica particle may contain the organic solvent mentioned later including water as an indispensable component. Although especially the presentation is not limited, it is required to be the presentation which organic polymer (P) dissolves. As the above-mentioned organic solvent, for example Aromatic hydrocarbon; methyl acetate, such as benzene, toluene, and a xylene, Ethyl acetate, propyl acetate, butyl acetate, isobutyl acetate, acetic-acid ethylene glycol monomethyl ether, Ester, such as acetic-acid ethylene glycol monoethyl ether and acetic-acid ethylene glycol monobutyl ether; An acetone, Ketones, such as a methyl ethyl ketone and methyl isobutyl ketone; A tetrahydrofuran, Ether, such as dioxane, ethyl ether, and G n-butyl ether; A methanol, Ethanol, isopropyl alcohol, n-butanol, ethylene glycol, Alcohols, such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, and ethylene glycol monobutyl ether; halogenated hydrocarbon, such as a methylene chloride and chloroform, is mentioned, and these two or more sorts may be mixed and used. Especially, since [which is mixed with water as making at least one sort indispensable and serves as uniform mixed liquor] it is chosen out of alcohols, ketones, and ether, an organic solvent is desirable.

[0029] As a catalyst used in case organic polymer (P) is hydrolyzed and condensed, a basic catalyst is desirable and this is Si-OR1 in organic polymer (P). It is because the invert ratio of a radical can be made higher and organic polymer can be firmly combined by the front face of a spherical silica particle. As a basic catalyst, alkali-metal-compound; basicity ion exchange resin, such as organic amine compound; sodium methoxide, such as ammonia; triethylamine and tripropylamine, a sodium ethoxide, a potassium methoxide, potassium ethoxide, potassium-tert-butoxide, a sodium hydroxide, and a potassium hydroxide, etc. is mentioned, and these two or more sorts may be mixed and used, for example. Especially, it is it easy to remove a basic catalyst after compound-izing to be ammonia and/or an organic amine compound, and it is desirable.

[0030] Although not limited especially about the blending ratio of coal, such as a spherical silica particle which is a raw material at the time of hydrolyzing and condensing, organic polymer (P), an organic solvent, a basic catalyst, and water, it is desirable in their being the following blending ratio of coal. Since the self-condensation of organic polymer (P) is prevented to the whole quantity of each raw material component, such as a spherical silica particle, organic polymer (P), an organic solvent, a basic catalyst, and water, as it is 0.1 - 30 % of the weight, the blending ratio of coal of a spherical silica particle is desirable, and it is 1 - 20 % of the weight most preferably 0.5 to 25% of the weight.

[0031] Since the self-condensation of organic polymer (P) is prevented to the whole quantity of a raw material component as it is 0.01 - 60 % of the weight, the blending ratio of coal of organic polymer (P) is desirable, and it is 0.2 - 20 % of the weight most preferably 0.1 to 50% of the weight. About the weight ratio (the organic (polymer P) / spherical silica particle) of organic polymer (P) and a spherical silica particle, since organic polymer (P) is efficiently combined with the front face of a spherical silica particle for example, as it is 0.01-1, compound-ization is performed and the self-condensation of organic polymer (P) is prevented, it is desirable. It is 0.05-0.7 more preferably and is 0.1-0.5 most preferably. When a weight ratio is larger than 1, organic polymer (P) may carry out self-condensation, and the condensate of organic polymer (P) may carry out a byproduction. There is too little organic polymer (P), and since it becomes that itis [compound-] hard to beized and this is not fully made, it becomes impossible on the other hand, for a spherical silica particle to give the outstanding compatibility over matrix resin etc. to the compound silica particle obtained, if a weight ratio is smaller than 0.01. In addition, although the self-condensation object with which organic polymer (P) carries out self-condensation, and they are obtained may be contained in the compound silica particle obtained after compound-izing, also in order to perform compound-ization more efficiently, it is desirable [the object] to perform hydrolysis and condensation in the range of the above-mentioned weight ratio.

[0032] Since homogeneity can be made to be able to distribute a spherical silica particle in dispersion liquid to the whole quantity of a raw material component as it is 0 - 99.9 % of the weight for example, and organic polymer (P) can fully be dissolved into dispersion liquid about the blending ratio of coal of an organic solvent, it is desirable, and it is 40 - 99 % of the weight most preferably 20 to 99% of the weight. It is [as opposed to / for example / blending ratio of coal / of a basic catalyst / the whole quantity of a raw material component] Si-OR1 in organic polymer (P) that it is 0.01 - 20 % of the weight. Since a radical can fully be hydrolyzed and condensed, it is desirable, and it is 0.1 - 5 % of the weight most preferably 0.05 to 10% of the weight.

[0033] If organic polymer (P) hydrolyzes and condenses, a spherical silica particle is compound-ized efficiently easily and a compound silica particle can be manufactured about the blending ratio of coal of water, it will not be limited especially, but as many, since organic polymer (P) hydrolyzes and becomes easy to condense the blending ratio of coal of water, it is more desirable. The blending ratio of coal of water is Si-OR1 hydrolyzed and condensed. It is three or more more preferably two or more 0.1 or more in a mole ratio to a radical. However, to water, when

insoluble, the blending ratio of coal of water is desirable to the whole quantity of a raw material component, and organic polymer (P) is 15 or less % of the weight most preferably 30 or less % of the weight 50 or less % of the weight.

[0034] The manufacture method of the compound silica particle of this invention is performed by hydrolyzing and condensing organic polymer (P) in the dispersion liquid which distributed the spherical silica particle. The reaction temperature is 0-100 degrees C, and is usually 0-70 degrees C preferably. Moreover, reaction time is usually 5 minutes - 100 hours, and hydrolysis and condensation are usually performed by stirring.

[0035] In the manufacture method of the compound silica particle of this invention, by mixing each raw material component, such as a spherical silica particle, organic polymer (P), an organic solvent, a basic catalyst, and water, organic polymer (P) hydrolyzes and condenses and compound-ization of a spherical silica particle is performed. Although especially the method of mixing each raw material component is not limited, a spherical silica particle, Each raw material component, such as organic polymer (P), an organic solvent, a basic catalyst, and water The mixture which could mix each in coincidence or sequence independently, could prepare beforehand the mixture which mixed some components, and could mix these mixture, and mixed some components, and an independent component may be mixed. Especially about the water which is a component required for making organic polymer (P) hydrolyze and condense, after making it contain beforehand in the dispersion liquid which distributed the spherical silica particle, making it contain in dispersion liquid separately from organic polymer (P) or organic polymer (P) and including organic polymer (P) in dispersion liquid, water may be included further. Moreover, the by-product generated by hydrolysis and condensation, a catalyst, etc. may be removed by filtration, distillation, etc.

[0036] After compound-izing a spherical silica particle in dispersion liquid as mentioned above, it is not necessary to remove water and the organic solvent which are contained in dispersion liquid, and to dry, neither condensation of the compound silica particle obtained nor the bridge formation between the compound silica particles by organic polymer (P) arises, and physical properties, such as particle diameter of the compound silica particle obtained, do not necessarily vary in order to fix organic polymer (P) on the front face of a spherical silica particle.

[0037] After the process of compound-izing, the compound silica particle obtained by the above-mentioned manufacture method remains as it is, and may be used as the below-mentioned compound silica particle dispersing element. After the process of compound-izing, the isolation process which separates a compound silica particle from the dispersion liquid after reacting may be established further. as an isolation process -- the dispersion liquid for example, after manufacture (dispersing element) -- a solvent with low compatibility with a compound silica particle -- in addition, a compound silica particle is settled and the isolation process to filter, the isolation process which distills off the dispersion medium which decompresses and heats the dispersion liquid after manufacture (dispersing element), and is contained in the dispersion liquid after manufacture are mentioned.

[0038] The compound silica particle of this invention is obtained by the above-mentioned manufacture method, and organic polymer is being fixed to the front face of a spherical silica particle main part through Si-O-Si association. Here, a spherical silica particle main part has the structure originating in a spherical silica particle, and organic polymer has the structure originating in the organic chain in organic polymer (P).

[0039] Although not limited especially about the rate of organic polymer to the whole compound silica particle, if there are too few rates of the organic polymer in a compound silica particle when it includes a compound silica particle in the plastic film of this invention mentioned later, compatibility with matrix resin etc. falls, a particle will come to drop out of the front face and the interior of a plastic film, and abrasion resistance will fall. On the other hand, if there are too many rates of organic polymer, physical properties which are the features of a silica, such as a degree of hardness and thermal resistance, will fall. For this reason, the rate of organic polymer is 2 - 30 % of the weight most preferably one to 40% of the weight still more preferably 0.1 to 60% of the weight preferably to the whole compound silica particle.

[0040] In the front face of the spherical silica particle main part in a compound silica particle, the organic radical and hydroxyl group originating in the spherical silica particle which is a raw material may remain, and the alkoxy group in the polysiloxane radical in the organic polymer (P) which is a raw material, the organic radical originating in the used organic solvent, etc. may remain on it.

[Compound silica particle dispersing element] The compound silica particle dispersing element of this invention is a dispersing element which the above-mentioned compound silica particle comes to distribute in dispersion liquid.

[0041] The organic solvent and water which were explained above are mentioned as a dispersion medium which constitutes dispersion liquid, and it is good also considering the mixture of an organic solvent and water as a dispersion medium. The blending ratio of coal of the compound silica particle contained in a compound silica particle dispersing element is 1 - 30 % of the weight most preferably 0.5 to 50% of the weight 0.1 to 60% of the weight preferably to the whole compound silica particle dispersing element. If the blending ratio of coal of a compound silica particle exceeds 60 % of the weight, the viscosity of a dispersing element will become high and it

will handling-come to be hard.

[0042] As a compound silica particle dispersing element, it sets to the manufacture method of the above-mentioned compound silica particle, for example. After manufacturing a compound silica particle by the thing and the above-mentioned manufacture method of a condition as it is, without isolating a compound silica particle, Once performing filtration, desiccation, etc. and isolating a compound silica particle, reduced pressure, heating, etc. carry out the thing which is mixed with a dispersion medium and manufactured, and the compound silica particle dispersing element obtained by the above-mentioned manufacture method again. Distilling off the dispersion medium at the time of manufacture of a compound silica particle, another dispersion medium is added and there are some which replace a dispersion medium and are manufactured.

[0043] Rather than the compound silica particle in the condition that isolation was carried out, a compound silica particle dispersing element has dramatically little condensation, and since it can treat in the condition of having distributed, it has the advantage that handling nature is high.

[Plastic film] The above-mentioned compound silica particle is the plastic film which it comes to distribute in matrix resin, and the plastic film of this invention contains the compound silica particle obtained by the above-mentioned manufacture method, and matrix resin.

[0044] Although not limited especially about matrix resin, acrylic resin (meta), polyethylene, polypropylene, a polyvinyl chloride, a polyvinylidene chloride, polyvinyl alcohol, polyester, a polycarbonate, polystyrene, an ethylene-vinyl acetate copolymer, etc. are mentioned, and these two or more sorts may be mixed and used, for example. Especially, since compatibility with the organic polymer in a compound silica particle becomes it high that they are acrylic resin (meta) and/or polyester, matrix resin is desirable.

[0045] Although not limited especially about the blending ratio of coal of the compound silica particle contained in a plastic film, it is 0.01 - 5 % of the weight most preferably 0.005 to 8% of the weight 0.001 to 10% of the weight preferably to the whole plastic film. Slipping nature, and hardness and anti blocking nature are no longer given to a plastic film as a compound silica particle is less than 0.001% of the weight of the whole plastic film. On the other hand, if it exceeds 10 % of the weight, in molding, a plastic film will become is hard to be obtained, and physical properties, such as the appearance, and reinforcement, smooth nature, will fall.

[0046] Although not limited especially about the method of manufacturing a plastic film, there is the manufacture method of next ** - **, for example.

** How to film-ize the constituent which mixes matrix resin and a compound silica particle and is obtained by the below-mentioned casting method, and to manufacture a plastic film.

** How to make the constituent which mixes the raw material and compound silica particle of matrix resin, and is obtained react, to film-ize by the below-mentioned casting method after changing matrix resin and a compound silica particle into the constituent mixed and obtained, and to manufacture a plastic film.

[0047] ** How to prepare beforehand the film containing the matrix resin used as a base material, and cover the front face of this film with the coating agent containing a compound silica particle.

Although not limited especially about the casting method used by the above-mentioned ** and **, the molding methods, such as a melting extrusion process, a ****** extrusion process, a tubular film process, a T-die method, the flow casting casting method, and the calender method, are mentioned, for example. Furthermore, after molding, a drawing, vacuum evaporationo, a lamination, a priming coat, etc. may be processed, and a plastic film may be manufactured.

[0048] In order to obtain the constituent of matrix resin and a compound silica particle by the above-mentioned **, after mixing with the above-mentioned compound silica particle dispersing element and matrix resin, it is necessary to remove the dispersion medium in a dispersing element by distillation etc. and, and an ultrasonic distribution machine, a homogenizer, etc. need to re-distribute a compound silica particle for isolation and the dried compound silica particle in matrix resin after mixing with matrix resin first. In addition, in the above-mentioned **, since the compound silica particle dispersing element which made the raw material of matrix resin distribute a compound silica particle is used, the clearance of a dispersion medium performed by the above-mentioned ** and the process which a compound silica particle re-distributes can be skipped.

[0049] The method of covering with the coating agent of the above-mentioned ** is the method of casting the matrix resin used as a base material, and processing a drawing, vacuum evaporationo, a lamination, a priming coat, etc. suitably, preparing a film, and covering the front face of this film with the coating agent containing a compound silica particle. In addition, a drawing, vacuum evaporationo, a lamination, etc. may be processed after a coat by the coating agent.

[0050] A coating agent contains an organic binder including a compound silica particle as an indispensable component. As an organic binder, if it has coat organization potency by itself Although not limited especially, the organic chain in a compound silica particle and the thing to dissolve are desirable. For example Polyolefines, such as

acrylic resin, polystyrene, polyvinyl acetate, polyethylene, and polypropylene, (Meta) Polyester, such as a polyvinyl chloride, a polyvinylidene chloride, and polyethylene terephthalate, And the resin which denaturalized in part by functional groups, such as these copolymers, and an amino group, an epoxy group, hydroxyl, a carboxyl group, is mentioned, and these two or more sorts may be mixed and used. Especially, compatibility with the organic polymer in a compound silica particle is high in organic binders being acrylic resin (meta) and/or polyester, and since there are no omission of the compound silica particle from a plastic film and sufficient slipping nature can be maintained for a long period of time, it is desirable.

[0051] The curing agent which stiffens an organic binder may be further included in a coating agent if needed. Although not limited especially about the method of covering with the coating agent in the above-mentioned **, it can carry out by the method of arbitration, such as a roller coat, a gravure coat, a DIP coat, and a spray coat, for example. Moreover, about the desiccation method after coating, and especially desiccation conditions, it is not limited and can carry out on the method of arbitration, and conditions.

[0052] According to the fitness in the above-mentioned coating method, and desired thickness, an above-mentioned organic solvent and/or water may be included in a coating agent as occasion demands. Any of the method of the above-mentioned ** - ** may be performed, and it is suitably chosen according to a condition. For example, when you want to skip the process which ** coats, when there is no equipment used for coating, a plastic film can be obtained by either method of ** and **. Moreover, when there are no making machines, such as an extruder, a plastic film can be obtained by the method of **.

[0053] Since the plastics film of this invention does not have omission of the compound silica particle from the front face and the interior, it has sufficient slipping nature and it excels in abrasion resistance, it can be used effective in a magnetic tape, an optical photographic film, a capacitor film, the film for hot printing printing, the film for a package, etc., and outstanding magnetic properties and performance traverse can be especially realized with the plastic film for magnetic tapes.

[Mat agent] The mat agent of this invention is a mat agent which comes to contain the above-mentioned compound silica particle, and is useful to silver halide sensitive material etc. including the compound silica particle obtained by the above-mentioned manufacture method.

[0054] When using the above-mentioned compound silica particle as a mat agent of for example, silver halide sensitive material, as a member of others which constitute silver halide sensitive material, a well-known thing can be used conventionally. namely, the increase of a base material and a resin binder -- photopigment -- as a surfactant, an ultraviolet ray absorbent, a plasticizer, a stabilizer, a hardening agent, a thickener, etc., the thing of arbitration can be used and the silver halide particle obtained by the method of arbitration can be used. Moreover, if needed, a magnetic-recording layer may be prepared or magnetic powder may be used together.

[0055] The mat agent of this invention can be used for at least one sort of layers chosen from the layer of the arbitration which constitutes silver halide sensitive material, for example, a base material, an under coat, an interlayer, an emulsion layer, a protective layer, etc. by the method of arbitration. although not limited especially about the amount of the mat agent used -- desirable -- 0.002 - 2 g/m2 it is -- more -- desirable -- 0.05 - 0.5 g/m2 it is .

[0056] Since the silver halide sensitive material obtained using the mat agent of this invention has the outstanding anti blocking nature, an image property, and stability and does not almost have omission of a mat agent, it is a good sensitive material.

[0057]

[Example] Although the concrete example of this invention is shown below, this invention is not limited to the following example. The example was performed after compounding a polymerization nature polysiloxane and organic polymer (P) by the examples 1-10 of the following manufacture.

(Example 1 of manufacture)

(Manufacture of a polymerization nature polysiloxane (S-1)) Tetramethoxy silane 144.5g, 23.6g [of gamma-methacryloxpropyl trimethoxy silane], 19g [of water], and methanol 30.0g and Amberlyst 15 (loam - and - Haas Japan cation exchange resin) 5.0g are put into the 300ml 4 opening flask equipped with the agitator, the thermometer, and the cooling pipe, and it stirred for 2 hours and was made to react at 65 degrees C. After cooling a reaction mixture to a room temperature, the cooling pipe and tap hole which replaced with the cooling pipe and were connected to a distilling column and this were prepared, and it held at this temperature until it applied for 2 hours, it carried out temperature up to 80 degrees C and a methanol stopped having flowed into the bottom of ordinary pressure. Furthermore, under the pressure of 200mmHg, at 90 degrees C, it held at this temperature until a methanol stopped having flowed out, and the reaction was advanced further. After cooling to a room temperature again, Amberlyst 15 was carried out the ** exception and number average molecular weight obtained the polymerization nature polysiloxane (S-1) of 1800.

(Example 2 of manufacture)
(Manufacture of organic polymer (P-1)) An agitator, dropping opening, a thermometer, a cooling pipe, and N2 200g of butyl acetate is put into the 1l. flask equipped with the gas inlet as an organic solvent, and it is N2. ** in a flask was heated to 120 degrees C, introducing and stirring gas. Subsequently, the solution which mixed polymerization nature polysiloxane (S-1) 20g [which was obtained in the example 1 of manufacture], methyl methacrylate 80g, 2-ethylhexyl acrylate 10g, styrene 60g, butyl acrylateg [30] and 2, and 2'-azobisisobutyronitril 6.5g was dropped over [opening / dropping] 2 hours. After dropping is after 1-hour stirring ****** and a 1 and 1'-screw (tert-butyl peroxide) at this temperature. - 3, 3, and 5-trimethyl cyclohexane 0.4g was added twice every 30 minutes, it heated for further 2 hours, copolymerization was performed, and number average molecular weight obtained the solution which the organic polymer (P-1) of 11,000 dissolved in butyl acetate. The solid content in the obtained solution was 49.0%.
(Example 3 of manufacture)
(Manufacture of organic polymer (P-2)) An agitator, dropping opening, a thermometer, a cooling pipe, and N2 Methanol 260g is put into the 500ml flask equipped with the gas inlet, and it is N2. ** in a flask was heated to 65 degrees C, introducing and stirring gas. Subsequently, polymerization nature polysiloxane (S-1) 14g obtained in the example 1 of manufacture, 2-hydroxyethyl acrylate 63g, polyoxyethylene methacrylate 63g and 2, and the solution that mixed 2'-azobis (2,4-dimethylvaleronitrile) 4g were dropped over [opening / dropping] 2 hours. After after dropping continued stirring at this temperature for 1 hour, 2 and 2'-azobis (2,4-dimethylvaleronitrile) 0.3g was added twice every 30 minutes, it heated for further 2 hours, copolymerization was performed, and number average molecular weight obtained the solution which the organic polymer (P-2) of 9,000 dissolved in the methanol. The solid content in the obtained solution was 35.0%.
(Examples 4-5 of manufacture)
(Manufacture of organic polymer (P-3 to P-4)) The solution which organic polymer (P-3 to P-4) dissolved in the methanol was obtained like the example 3 of manufacture except changing into the presentation shown in a table 1. The number average molecular weight of the obtained organic polymer (P-3 to P-4) and the solid content in a solution are shown in a table 1.
[0058]
[A table 1]

	有機ポリマー (P)	開始剤 (g)	溶媒 (g)	モノマー組成 (g)									固形分 (wt%)	数平均分子量
				MMA	2-EHMA	St	BA	HEA	HEMA	POEMA	AA	S-1		
製造例2	P－1	AIBN 6.5	酢酸ブチル 200	80	10	60	30					20	49.0	11,000
製造例3	P－2	ADVN 4.0	メタノール 260					63		63		14	35.0	9,000
製造例4	P－3	ADVN 4.0	メタノール 260	63							63	14	35.5	10,000
製造例5	P－4	ADVN 4.0	メタノール 260						63	63		14	35.0	8,500

[0059] azobisuisobutironitoriru: 2, 2'-azobisisobutyronitril ADVN:2, 2'-azobis (2,4-dimethylvaleronitrile) MMA:methyl methacrylate 2-EHA: -- 2-ethylhexyl acrylate St:styrene HEA:2-hydroxyethyl acrylate HEMA:2-hydroxyethyl methacrylate POEMA: -- a polyoxymethylene methacrylate AA:acrylic-acid S-1:polymerization nature polysiloxane (S-1)
(Example 6 of manufacture)
(Manufacture of a spherical silica particle distribution solvent (D-1)) 511g [of butyl acetate] and methanol 128g is put into the 1l. 4 opening flask equipped with an agitator, two dropping openings (dropping opening I and dropping opening RO), and a thermometer, and inside ** was adjusted to 20 degrees C. Subsequently, 41g [of water from dropping opening I], 14g [of 25% aqueous ammonia], and methanol 55g mixed liquor was dropped for tetramethoxy silane 108g over 40 minutes from dropping opening RO, stirring the inside of a flask. Stirring was continued at this temperature after dropping for 1 hour, and the spherical silica particle distribution solvent (D-1) was obtained. The liquid presentation of the mean particle diameter of the obtained spherical silica particle, coefficient of variation, and a spherical silica particle distribution solvent (D-1) is shown in a table 2.
[0060] In addition, the mean particle diameter of a spherical silica particle and the below-mentioned compound silica particle and coefficient of variation were measured by the following methods.
(Mean particle diameter and coefficient of variation) The particle was photoed with the transmission electron microscope, the diameter of 100 particles of arbitration was read, and the average was made into mean particle diameter. Moreover, coefficient of variation was computed by the following formula.

[0061] Coefficient of variation (%) =(standard deviation of particle diameter of particle)/(mean particle diameter of a particle)

(Example 7 of manufacture)

(Manufacture of a spherical silica particle distribution solvent (D-2)) the 1l. Mayer flask equipped with the agitator and the ultrasonic homogenizer -- methanol 696g and NIPPON SHOKUBAI Make -- spherical -- silica particle fine-particles "SHIHO star KE-P100" 24g was put in, and ultrasonic distribution was performed for 1 hour. Subsequently, 80g of aqueous ammonia was added, stirring was performed at the room temperature for 1 hour, and the spherical silica particle distribution solvent (D-2) was obtained. The liquid presentation of the mean particle diameter of the spherical silica particle in the obtained solvent, coefficient of variation, and a spherical silica particle distribution solvent (D-2) is shown in a table 2.

(Example 8 of manufacture)

(Manufacture of a spherical silica particle distribution solvent (D-3)) The spherical silica particle distribution solvent (D-3) was obtained like the example 7 of manufacture except using "SHIHO star KE-P250" By NIPPON SHOKUBAI as spherical silica particle fine particles. The liquid presentation of the mean particle diameter of the spherical silica particle in the obtained solvent, coefficient of variation, and a spherical silica particle distribution solvent (D-3) is shown in a table 2.

(Example 9 of manufacture)

(Manufacture of a spherical silica particle distribution solvent (D-4)) Methanol 229g and 36g of 25% aqueous ammonia are put into the 500ml 4 opening flask equipped with an agitator, two dropping openings (dropping opening I and dropping opening RO), and a thermometer, and inside ** was adjusted to 20 degrees C. Subsequently, 17g of dropping opening I to water was dropped for tetramethoxy silane 73g over 40 minutes from dropping opening RO, stirring the inside of a flask. Stirring was continued at this temperature after dropping for 1 hour, and the spherical silica particle distribution solvent (D-4) was obtained. The liquid presentation of the mean particle diameter of the obtained spherical silica particle, coefficient of variation, and a spherical silica particle distribution solvent (D-4) is shown in a table 2.

(Example 10 of manufacture)

(Manufacture of a spherical silica particle distribution solvent (D-5)) the 1l. Mayer flask equipped with the agitator -- methanol 688g and the Nissan Chemical Industries, Ltd. make -- "Snow tex C" 40g and 72g of aqueous ammonia were put in, stirring was performed for 1 hour, and the spherical silica particle distribution solvent (D-5) was obtained. The liquid presentation of the mean particle diameter of the spherical silica particle in the obtained solvent, coefficient of variation, and a spherical silica particle distribution solvent (D-5) is shown in a table 2.

[0062]

[A table 2]

	球状シリカ微粒子分散溶媒	球状シリカ微粒子分散溶媒の組成 (wt%)					平均粒子径 (μm)	変動係数 (%)
		シリカ 微粒子	メタノール	酢酸ブチル	水	アンモニア		
製造例6	D－1	5.0	31.9	59.7	3.0	0.4	0.8	12
製造例7	D－2	3.0	87.0		7.5	2.5	1.0	7
製造例8	D－3	3.0	87.0		7.5	2.5	2.5	6
製造例9	D－4	8.1	81.9		7.5	2.5	0.2	14
製造例10	D－5	1.0	86.0		10.7	2.3	0.02	50

[0063] (Example A1)

(Manufacture of a compound silica particle (Z-1) dispersing element) 350g (D-1) of spherical silica particle distribution solvents obtained in the example 6 of manufacture is put into the 500ml 4 opening flask equipped with an agitator, dropping opening, and a thermometer, and inside ** was adjusted to 20 degrees C. Subsequently, 4.5g of butyl-acetate solutions of the organic polymer (P-1) obtained in the example 2 of manufacture and the mixed liquor of 4.5g of butyl acetate were dropped over 20 minutes, stirring the inside of a flask. Stirring was continued at this temperature after dropping for 1 hour. Temperature up of the ** in a flask was carried out to the pan to 100 degrees

C under the pressure of 110mmHg(s), ammonia, a methanol, water, and butyl acetate were distilled off until solid content became 25%, and the butyl-acetate dispersing element of a compound silica particle (Z-1) was obtained. The mean particle diameter of the obtained compound silica particle (Z-1), coefficient of variation, and the silica concentration in this particle are shown in a table 3.

[0064] In addition, the mean particle diameter and coefficient of variation of a compound silica particle were measured by the above-mentioned method. Moreover, the silica concentration in a compound silica particle was measured by the following methods.

(Silica concentration in a compound silica particle) Elemental analysis was performed about the compound silica particle fine particles obtained by drying a compound silica particle dispersing element, and ash content was computed as a silica.

(Example A2)

(Manufacture of a compound silica particle (Z-2) dispersing element) 380g (D-2) of spherical silica particle distribution solvents obtained in the example 7 of manufacture is put into the 500ml 4 opening flask equipped with an agitator, dropping opening, and a thermometer, and inside ** was adjusted to 20 degrees C. Subsequently, 4g of methanol solutions of the organic polymer (P-2) obtained in the example 3 of manufacture and methanol 4g mixed liquor were dropped over 20 minutes, stirring the inside of a flask. Stirring was continued at this temperature after dropping for 1 hour. Temperature up of the ** in a flask was carried out to the pan to 125 degrees C under the pressure of 60mmHg(s), it condensed until ethylene glycol 103g was dropped and solid content became 10%, distilling off ammonia, a methanol, and water, and the ethylene glycol dispersing element of a compound silica particle (Z-2) was obtained. The mean particle diameter of the obtained compound silica particle (Z-2), coefficient of variation, and the silica concentration in this particle are shown in a table 3.

(Example A3)

(Manufacture of a compound silica particle (Z-3) dispersing element) 380g (D-3) of spherical silica particle distribution solvents obtained in the example 8 of manufacture is put into the 500ml 4 opening flask equipped with an agitator, dropping opening, and a thermometer, and inside ** was adjusted to 20 degrees C. Subsequently, 9.2g of methanol solutions of the organic polymer (P-3) obtained in the example 4 of manufacture and methanol 9.2g mixed liquor were dropped over 20 minutes, stirring the inside of a flask. Stirring was continued at this temperature after dropping for 1 hour. Temperature up of the ** in a flask was carried out to the pan to 125 degrees C under the pressure of 60mmHg(s), it condensed until ethylene glycol 103g was dropped and solid content became 10%, distilling off ammonia, a methanol, and water, and the ethylene glycol dispersing element of a compound silica particle (Z-3) was obtained. The mean particle diameter of the obtained compound silica particle (Z-3), coefficient of variation, and the silica concentration in this particle are shown in a table 3.

(Example A4)

(Manufacture of a compound silica particle (Z-4) dispersing element) 350g (D-4) of spherical silica particle distribution solvents obtained in the example 9 of manufacture is put into the 500ml 4 opening flask equipped with an agitator, dropping opening, and a thermometer, and inside ** was adjusted to 20 degrees C. Subsequently, 16g of methanol solutions of the organic polymer (P-4) obtained in the example 5 of manufacture and methanol 16g mixed liquor were dropped over 20 minutes, stirring the inside of a flask. Stirring was continued at this temperature after dropping for 1 hour. Temperature up of the ** in a flask was carried out to the pan to 125 degrees C under the pressure of 60mmHg(s), it condensed until ethylene glycol 257g was dropped and solid content became 10%, distilling off ammonia, a methanol, and water, and the ethylene glycol dispersing element of a compound silica particle (Z-4) was obtained. The mean particle diameter of the obtained compound silica particle (Z-4), coefficient of variation, and the silica concentration in this particle are shown in a table 3.

(Example A5)

(Manufacture of a compound silica particle (Z-5) dispersing element) 380g (D-5) of spherical silica particle distribution solvents obtained in the example 10 of manufacture is put into the 500ml 4 opening flask equipped with an agitator, dropping opening, and a thermometer, and inside ** was adjusted to 20 degrees C. Subsequently, 1.5g of methanol solutions of the organic polymer (P-2) obtained in the example 3 of manufacture and methanol 6.5g mixed liquor were dropped over 20 minutes, stirring the inside of a flask. Stirring was continued at this temperature after dropping for 1 hour. Temperature up of the ** in a flask was carried out to the pan to 125 degrees C under the pressure of 60mmHg(s), it condensed until ethylene glycol 34g was dropped and solid content became 10%, distilling off ammonia, a methanol, and water, and the ethylene glycol dispersing element of a compound silica particle (Z-5) was obtained. The mean particle diameter of the obtained compound silica particle (Z-4), coefficient of variation, and the silica concentration in this particle are shown in a table 3.

(Example A6)

(Manufacture of a compound silica particle (Z-6)) 330g (D-2) of spherical silica particle distribution solvents

obtained in the example 7 of manufacture is put into the 500ml 4 opening flask equipped with an agitator, dropping opening, and a thermometer, and inside ** was adjusted to 20 degrees C. Subsequently, 30g of methanol solutions of the organic polymer (P-2) obtained in the example 3 of manufacture and methanol 30g mixed liquor were dropped over 40 minutes, stirring the inside of a flask. Stirring was continued at this temperature after dropping for 1 hour. Furthermore, temperature up of the ** in a flask was carried out to 70 degrees C under ordinary pressure, and ammonia, a methanol, and water were distilled off, and it condensed until solid content became 30%. Furthermore, it held at 120 degrees C under the pressure of 50mmHg(s) within the vacuum drier for 2 hours, and the desiccation object of a compound silica particle (Z-6) was acquired. The mean particle diameter of the obtained compound silica particle (Z-6), coefficient of variation, and the silica concentration in this particle are shown in a table 3.
[0065]
[A table 3]

	複合シリカ微粒子	製造に使用した球状シリカ微粒子分散溶媒	製造に使用した有機ポリマー	複合シリカ微粒子中のシリカ濃度(wt%)	平均粒子径(μm)	変動係数(%)
実施例A1	Z−1	D−1	P−1	90	0.8	13
実施例A2	Z−2	D−2	P−2	90	1.0	7
実施例A3	Z−3	D−3	P−3	80	2.5	5
実施例A4	Z−4	D−4	P−4	85	0.2	14
実施例A5	Z−5	D−5	P−2	85	0.02	48
実施例A6	Z−6	D−2	P−2	52	1.0	9

[0066] (Example A1 of a comparison)
(Surface treatment of a spherical silica particle) 380g (D-2) of spherical silica particle distribution solvents obtained in the example 7 of manufacture is put into the 500ml 4 opening flask equipped with an agitator, dropping opening, and a thermometer, and inside ** was adjusted to 20 degrees C. Subsequently, mixed liquor (methyl trimetoxysilane 4g and methanol 4g) was dropped over 30 minutes, stirring the inside of a flask. Stirring was continued at this temperature after dropping for 1 hour. Into the obtained liquid, the minute particle was newly in addition to the spherical silica particle obtained in the example 7 of manufacture generating, and surface treatment of a spherical silica particle was not able to be performed well.
(Example A2 of a comparison)
(Surface treatment of a spherical silica particle) the 1l. Mayer flask equipped with the agitator and the ultrasonic homogenizer -- methanol 696g and NIPPON SHOKUBAI Make -- spherical -- silica particle fine-particles "SHIHO star KE-P100" 24g was put in, and ultrasonic distribution was performed for 1 hour. Subsequently, methyl trimetoxysilane 0.2g was added and stirring was performed at the room temperature for 1 hour. Stoving was carried out at 120 degrees C under the pressure of 50mmHg(s) within the vacuum drier for 24 hours, and the surface treatment article fine particles (Z' - 1) of a spherical silica particle were obtained.
(Example A3 of a comparison)
(Manufacture of a spherical silica particle dispersing element) the 300ml Mayer flask equipped with the agitator and the ultrasonic homogenizer -- NIPPON SHOKUBAI Make -- spherical -- silica particle fine-particles "SHIHO star KE-P100" 20g and ethylene glycol 180g were put in, and ultrasonic distribution was performed for 1 hour. Subsequently, stirring was performed at the room temperature for 1 hour, and the spherical silica particle ethylene glycol dispersing element was obtained.
(Example A4 of a comparison)
(Manufacture of a spherical silica particle dispersing element) The spherical silica particle ethylene glycol dispersing element was obtained like the example A1 of a comparison except using the surface treatment article fine particles (Z' - 1) of the spherical silica particle obtained in the example A2 of a comparison.
(Example B1)
(Manufacture of a plastic film (F-1)) 1g (Z-1) of butyl-acetate dispersing elements of the compound silica particle

obtained in the example 1 of manufacture, and NIPPON SHOKUBAI Make -- polyester resin "AROPU long acting thuroid stimulator BO-110" 15g and 400g of butyl acetate were mixed, and it considered as spreading liquid. This spreading liquid was applied to one side of a polyethylene terephthalate film by the bar coating machine, and it dried at 140 degrees C with the room temperature for 20 minutes for 20 minutes. The test result about the slipping nature (dynamic friction coefficient) of the obtained plastic film (F-1) and abrasion resistance, and the compatibility of the compound silica particle in a plastic film and the resin which constitutes a film is shown in a table 4. The slipping nature of the obtained plastic film, abrasion resistance, and compatibility were good.

[0067] In addition, assessment of a plastic film was performed by the following methods.

(Dynamic friction coefficient) The film was cut to 200x100mm, and it measured with following equipment. Product made from HEIDON Continuation load type front-face nature measurement machine A 20g load is applied to the ends of a film with a TYPE:HEIDON-22 (abrasion resistance) length [of 40cm], and a width of face of 15mm, it went and came back to the pin made from stainless steel with a diameter of 5mm 200 times, and it was made to rub on 150 bending squares.

[0068] The existence of a scratch was observed externally and the thing of whenever [x and its middle] was made [what does not almost have a scratch] into ** for O and what has many scratches.

(Compatibility) After investigating the above-mentioned abrasion resistance, the front face of a film was observed with the scanning electron microscope, and the thing of whenever [x and its middle] was made into ** for what has many omission of O and a particle by what does not almost have omission of a particle.

(Example B-2)

(Manufacture of a plastic film (F-2)) 1g (Z-1) of butyl-acetate dispersing elements of the compound silica particle obtained in the example 1 of manufacture, and NIPPON SHOKUBAI Make -- acrylic resin "AROTAN 2060" 15g and the Sumitomo Chemical Co., Ltd. make -- isocyanate curing agent "Sumi Joule N-3500" 2.5g and 400g of butyl acetate were mixed, and it considered as spreading liquid. This spreading liquid was applied to one side of a polyethylene terephthalate film by the bar coating machine, and it dried at 80 degrees C with the room temperature for 40 minutes for 30 minutes. The test result about the slipping nature (dynamic friction coefficient) of the obtained plastic film (F-2), abrasion resistance, and compatibility is shown in a table 4.

(Example B3)

(Manufacture of a plastic film (F-3)) 1g (Z-1) of butyl-acetate dispersing elements of the compound silica particle obtained in the example 1 of manufacture, and NIPPON SHOKUBAI Make -- acrylic resin "you double S-5140SPL"15g and 400g of butyl acetate were mixed, and it considered as spreading liquid. This spreading liquid was applied to one side of a polyethylene film by the bar coating machine, and it dried at 60 degrees C with the room temperature for 40 minutes for 20 minutes. The test result about the slipping nature (dynamic friction coefficient) of the obtained plastic film (F-3), abrasion resistance, and compatibility is shown in a table 4.

(Example B1 of a comparison)

(Manufacture of a plastic film (F' - 1)) NIPPON SHOKUBAI Make -- spherical -- silica particle fine-particles "SHIHO star KE-P100" 0.5g and NIPPON SHOKUBAI Make -- ultrasonic distribution was carried out for 30 minutes, and spreading liquid took after mixing polyester resin "AROPU long acting thuroid stimulator BO-110" 30g and 800g of butyl acetate. This spreading liquid was applied to one side of a polyethylene terephthalate film by the bar coating machine, and it dried at 140 degrees C with the room temperature for 20 minutes for 20 minutes. The test result about the slipping nature (dynamic friction coefficient) of the obtained plastic film (F' - 1), abrasion resistance, and compatibility is shown in a table 4.

(Example B-2 of a comparison)

(Manufacture of a plastic film (F' - 2)) The plastic film (F' - 2) was obtained like the example B1 of a comparison except using 0.5g (Z' - 1) of surface treatment article fine particles of the spherical silica particle obtained in the example A2 of a comparison as a spherical silica particle. The test result about the slipping nature (dynamic friction coefficient) of the obtained plastic film (F' - 2), abrasion resistance, and compatibility is shown in a table 4.

(Example B4)

(Manufacture of a plastic film (F-4)) 0.04g of manganese acetate 4 hydrates was added to dimethyl terephthalate 100g and ethylene glycol 70g as a catalyst, temperature up was carried out to the 500ml 4 opening flask equipped with the distilling column which the agitator, the thermometer, the cooling pipe, and the tap hole connected to 230 degrees C, the methanol was distilled off, and the ester exchange reaction was performed. Subsequently, after adding stirring 3g of ethylene glycol dispersing elements and 0.03g of antimony trioxides of a compound silica particle (Z-2) obtained in the example A2, under the pressure of 1mmHg, temperature up was carried out to 280 degrees C, the polycondensation was performed, and polyester resin was obtained. This polyester resin was extruded in the shape of a sheet with the extruder set as 290 degrees C, and subsequently to a longitudinal direction, it extended after extending 3.5 times to a lengthwise direction at 90 degrees C, and extended 4 times at 100 degrees C,

heat treatment was performed for 10 seconds at 210 degrees C, and the plastic film (F-4) was obtained. The slipping nature of a plastic film and abrasion resistance which were obtained were good. The test result about the slipping nature (dynamic friction coefficient) of the obtained plastic film (F-4), abrasion resistance, and compatibility is shown in a table 4.
(Example B5-B7)
(Manufacture of a plastic film (F-5 to F-7)) The plastic film (F-5 to F-7) was obtained like example B4 except using the ethylene glycol dispersing element of the compound silica particle shown in a table 4. The test result about the slipping nature (dynamic friction coefficient) of the obtained plastic film (F-5 to F-7), abrasion resistance, and compatibility is shown in a table 4.
(The example B3 of a comparison - B4)
(Manufacture of a plastic film (F' - 3-F' - 4)) The plastic film (F' - 3-F' - 4) was obtained like example B4 except using the spherical silica particle ethylene glycol dispersing element obtained by example A3 of a comparison, and example A4 of a comparison. The test result about the slipping nature (dynamic friction coefficient) of the obtained plastic film (F' - 3-F' - 4), abrasion resistance, and compatibility is shown in a table 4.
(Example B8)
(Manufacture of a plastic film (F-8)) The 3 sections of desiccation objects of the compound silica particle (Z-6) obtained in the example A6 were blended to the polypropylene ((melt-flow-index MI) 2g /, 10-minute, 3% of heptane extractives) 97 section, it scoured at 230 degrees C with the Banbury mixer, and the pellet was obtained. Subsequently, this pellet 10 section and the polypropylene 90 above-mentioned section were mixed, and it extruded in the shape of a sheet with the extruder set as 260 degrees C, and subsequently, it is at this temperature after extending 5 times to a lengthwise direction in 175 degrees C, and extended 9 times in the longitudinal direction, and the plastic film (F-8) was obtained. The test result about the slipping nature (dynamic friction coefficient) of the obtained plastic film (F-8), abrasion resistance, and compatibility is shown in a table 4.
(Example B9)
(Manufacture of a plastic film (F-9)) The 5 sections of desiccation objects of the compound silica particle (Z-6) obtained in the example 6 were blended to the low-density-polyethylene ((melt-flow-index MI) 2g /, 10-minute, density 0.92g/cm3) 95 section, it scoured at 220 degrees C with the Banbury mixer, and the pellet was obtained. Subsequently, this pellet 8 section and the polyethylene 92 above-mentioned section were mixed, it extruded from the T die in the shape of a sheet with the extruder set as 200 degrees C, and the plastic film (F-9) was obtained. The test result about the slipping nature (dynamic friction coefficient) of the obtained plastic film (F-9), abrasion resistance, and compatibility is shown in a table 4.
[0069]
[A table 4]

	プラスチックフィルム	複合シリカ微粒子または球状シリカ微粒子	滑り性・動摩擦係数	耐磨耗性	親和性
実施例Ｂ１	Ｆ－１	Ｚ－１	0.24	○	○
実施例Ｂ２	Ｆ－２	Ｚ－１	0.23	○	○
実施例Ｂ３	Ｆ－３	Ｚ－１	0.26	△	○
実施例Ｂ４	Ｆ－４	Ｚ－２	0.15	○	○
実施例Ｂ５	Ｆ－５	Ｚ－３	0.12	○	○
実施例Ｂ６	Ｆ－６	Ｚ－４	0.23	○	○
実施例Ｂ７	Ｆ－７	Ｚ－５	0.28	○	○
実施例Ｂ８	Ｆ－８	Ｚ－１	0.18	○	○
実施例Ｂ９	Ｆ－９	Ｚ－１	0.24	○	○
比較例Ｂ１	Ｆ’－１	シーホスターKE-P100	0.25	×	×
比較例Ｂ２	Ｆ’－２	Ｚ’－１	0.23	△	△
比較例Ｂ３	Ｆ’－３	シーホスターKE-P100	0.16	×	×
比較例Ｂ４	Ｆ’－４	Ｚ’－１	0.17	△	△

[0070] (Example C1) The silver chloride crystal with a mean particle diameter of 0.3 micrometers was processed with 0.05-N potassium iodide solution, and the obtained precipitate was refined. What was processed with chloroauric acid after remelting, and 4-hydroxy-6-methyl - 1, 3, and 3a-7-tetra-ZAIDEN, the surfactant, and the hardening agent were mixed, and the emulsion was prepared. The coat of this emulsion was carried out on the polyethylene terephthalate film (PET film), and the emulsion layer was made to form on a PET film. Furthermore, 1g (Z-6) of compound silica particles and gelatin 10g obtained in the example A6 were distributed in 100g of water, and the mat agent content constituent was obtained. The coat of this mat agent content constituent was carried out on the emulsion layer, and the trial film was obtained. in addition, the amount of the mat agent used -- 0.025 g/m2 it was .

[0071] The good image was obtained when the above-mentioned trial film was developed with the conventional method after test pattern exposure. Furthermore, the following methods estimated anti blocking nature and a mat agent maintenance property.

(Anti blocking nature) Five peeling condition of the trial film of ******** was investigated for the trial film before development after one-week standing at 25 degrees C in piles. O and the thing which cannot peel a little easily were judged to be **, and the trial film judged what cannot peel easily for what peeled finely to be x.

(Mat agent maintenance property) After cutting the trial film before development in width of face of 5cm, and length of 30cm and twisting around a stainless steel shaft with a diameter of 1cm, the shaft was rolled at the rate of 1 cm/sec, and the film was stripped. After repeating this actuation 10 times, the amount of the mat agent which is on a film with an optical microscope was investigated. That by which a mat agent hardly remains that in which the mat agent almost remains in O and reverse was judged to be x, and these middle things were judged to be **.

[0072] All of the anti blocking nature of the trial film of the above-mentioned example C1 and a mat agent maintenance property were O.

(Example C1 of a comparison) It replaced with the compound silica particle (Z-6) obtained in the example A6, and the comparative study film was obtained like the example C1 except using the spherical silica particle fine particles "SHIHO star KE-P100" by NIPPON SHOKUBAI Co., Ltd. The good image was obtained when the trial film was developed with the conventional method after test pattern exposure. Furthermore, although the anti blocking nature was O, the mat agent maintenance property was **.

[0073]

[Effect of the Invention] The compound silica particle of this invention has the compatibility which was excellent to matrix resin, it is the compound silica particle which does not have variation in physical properties, and the manufacture method of the compound silica particle of this invention can manufacture this compound silica particle easily. Without making a compound silica particle condense, the compound silica particle dispersing element of this invention can be treated in the condition of having distributed, and is excellent in handling nature.

[0074] The plastic film of this invention does not have omission of a compound silica particle, has sufficient slipping nature, and is excellent in abrasion resistance. Therefore, a plastic film can be used for a magnetic tape, an optical photographic film, a capacitor film, the film for hot printing printing, the film for a package, etc., and magnetic properties and performance traverse which were excellent in the plastic film for magnetic tapes especially can be realized.

[0075] The mat agent of this invention can give the outstanding anti blocking nature, and does not drop out easily. Furthermore, if this mat agent is used for silver halide sensitive material, an image property, stability, etc. can be given.